

# THERMAL CRACKING PROPERTY OF MARLIM VACUUM RESIDUE

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## INTRODUCTION

The world-wide demand for transportation fuels and light fraction oils is expected to increase steadily, while the world supply crude has become rather heavier. Therefore, development of the upgrading technology of heavy oils is very important. However, upgrading of heavy oils is generally very difficult because of serious problems such as coke formation and catalyst deactivation. These problems are mainly caused by asphaltene in heavier oil. In catalytic hydrocracking of heavy oils, asphaltenes are known to be the most refractory. It is profitable for the progress of upgrading of heavy oils such as vacuum residue to understand the reaction behavior of asphaltene cracking. Many investigators provide ample information about pathways, kinetics and coke formation mechanism in the thermal cracking of asphaltenes or residues<sup>1-9</sup>. The purpose of this study is to clarify thermal cracking behavior of Brazilian Marlim vacuum residue, its asphaltene and deasphalted oil. Marlim crude is Brazil off-shore of large scale reservoir and a typical heavy oil. The vacuum residue in Marlim crude is as many as 30-33% and has high asphaltene contents.

## EXPERIMENTAL

Feed materials used in this study were Marlim vacuum residue(MLVR) and the asphaltene (MLVR-AS) and the deasphalted oil (MLVR-DAO) obtained from MLVR. MLVR-AS was precipitated with excess of n-heptane (40:1), stirred for 24 hours and separated with a centrifuge. Finally, the asphaltene was dried under vacuum at 50°C, for 24 hours. MLVR-DAO was obtained from n-heptane solubles by removing n-heptane with evaporator.

A 110 ml batch autoclave with magnetic stirrer was used in the thermal cracking. An autoclave was loaded with 3 g of feed and 15 g of decalin as solvent and pressurized to 1 MPa of nitrogen gas and heated up to the reaction temperature(400-440°C) at 10°C/min. After holding at reaction temperature for the desired time(0-90 min), the autoclave was cooled down to room temperature and gases were vented off and analyzed by gas chromatography. The reaction products in the autoclave were separated into the oil and the solid products by suction filtration. The solid product was extracted with toluene using ultra sonic. Toluene insoluble material in the solid product was defined as coke.

<sup>1</sup>H and <sup>13</sup>C NMR were measured using JEOL Lamda 500. The conceptual structure model of asphaltene samples were deduced from the structural parameters obtained from NMR, elemental analyses and average molecular weight with the proposed by Sato's method<sup>10</sup>.

## RESULTS AND DISCUSSION

The properties of three Marlim samples (MLVR, MLVR-DAO and MLVR-AS) and Arabian Light vacuum residue asphaltene (ALVR-AS) are shown in Table 1. Nitrogen content of MLVR-AS is about twice of DAO and nitrogen is concentrated in the asphaltene fraction. On the other hand, sulfur contents of asphaltene and deasphalted oil are almost the same. On the comparison between MLVR-AS and ALVR-AS, nitrogen content of MLVR-AS is higher than ALVR-AS, but the content of sulfur and vanadium is lower than ALVR-AS. H/C atomic ratios and fa of MLVR-AS is similar to ALVR-AS.

Coking property of MLVR, MLVR-DAO and MLVR-AS are shown in Figure 1. Coke yield from MLVR-AS increased rapidly from 410°C of cracking temperature. In contrast, the coke formation from DAO did not take place even 420°C. But asphaltene were observed to form in the product oil after thermal cracking of MLVR-DAO. The coke yield from MLVR corresponded to the total amount of coke generated from asphaltene fraction and maltene fraction in MLVR. Asphaltene fraction are easily caused the coke formation during the thermal cracking.

Figure 2 shows the relationship between the reaction time and the coke yield in thermal cracking of MLVR-AS at the various temperatures. When cracking temperature was 410°C, The coke formation was not observed until 30 min of the reaction time and seemed to have an induction period. On the other hand, at higher temperature (430, 440°C), coke was formed rapidly at high rate without an induction period. This tendency was observed in thermal cracking of ALVR-AS<sup>11)</sup>.

Gas yield from MLVR-AS cracking is shown in Table 2. H<sub>2</sub> and hydrocarbon gases increased with an increase of reaction severity (temperature and time). It seems that coking of asphaltene progresses attended with dehydrogenation and dealkylation. A small amount of CO and CO<sub>2</sub> were observed in the generated gases. CO<sub>2</sub> yield was almost constant regardless of the reaction conditions. CO<sub>2</sub> formation suggests asphaltene molecule has carboxylic functionality and decarboxylation is finished at the initial stage of the reaction.

The composition and structure of original asphaltene were changed with thermal cracking. Elemental analyses and molecular weight and NMR spectra of reacted asphaltene were measured. The H/C atomic ratios and molecular weight of reacted asphaltenes decreased with an increase of the cracking temperature (Figure 3). Especially, the molecular weight of reacted asphaltene decreased rapidly with an increase of the reaction severity. Structural parameters of original asphaltene (MLVR-AS) and reacted asphaltene are shown in Table 3.

Figure 4 shows the conceptual model structure of original asphaltene and reacted asphaltene at 400, 430 and 440°C of the cracking temperature. As shown in this picture (figure 4), at low cracking temperature(400°C), asphaltene decomposition occurs through the cleavage of bridge chain which connects the cluster unit structure in asphaltene molecule. At higher temperature, in addition to the cleavage of bridge chain, dealkylation of alkyl substitutes connected to fused ring and dehydrogenation of naphthenic ring are found to be occurred. The reacted asphaltene obtained at 440°C was almost composed of fused aromatic ring.

## CONCLUSION

This work was carried out to investigate the thermal cracking behavior of Barazilan Marlum vacuum residue.

1. Marlum vacuum residue has relatively high CCR, asphaltenes and nitrogen. Nitrogen compounds are concentrated in the asphaltene fraction. The asphaltene from VR has high aromaticity.
2. Coking reaction of the asphaltene was caused rapidly from 410°C. For deasphalted oil from VR, the formation of coke was not observed even at the temperature of 420°C.
3. Molecular weight and H/C atomic ratios of reacted asphaltene decreased with an increase of the cracking temperature. Asphaltene reacted at higher temperature shows highly aromatic structure with a little alkyl substitutes.

## ACKNOWLEDGMENT

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Table 1 Properties of Marlim Vacuum Residues

	MLVR	MLVR-DAO	MLVR-AS	ALVR-AS*
C (wt%)	86.66	86.59	87.12	83.94
H (wt%)	10.17	10.88	8.62	7.86
N (wt%)	0.98	0.72	1.49	0.95
S (wt%)	0.90	0.88	1.04	6.72
H/C (atm)	1.40	1.50	1.18	1.12
V (ppm)	82	43	230	466
Ni (ppm)	59	33	160	128
n-C7 15 (wt%)	21.4			
C.C.R. (wt%)	22.8	15.7		
fa	0.30	0.26	0.45	0.42

\* ALVR-AS : Arabian Light Asphaltene

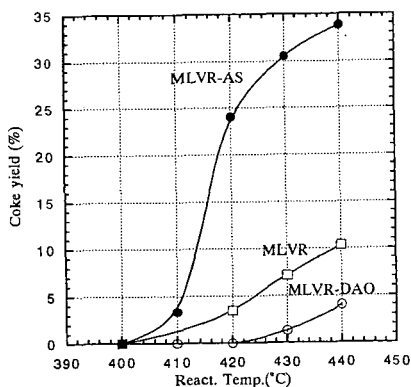


Figure 1. Coking property of Marlim vacuum residues

N<sub>2</sub>: 1MPa, Feed/DH=3/15wt, React. time : 60 min

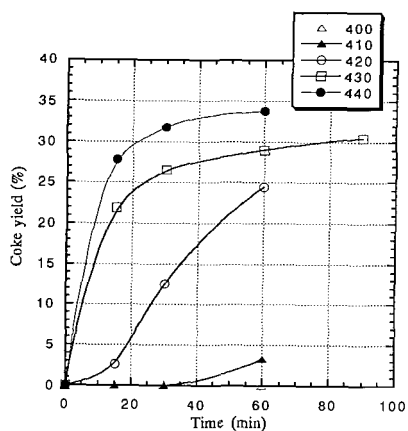


Figure 2. Effect of reaction time on coke formation of MLVR-AS thermal cracking

Table 2 Reaction conditions and gas distribution from MLVR-AS thermal cracking

Conditions		Yield (wt%/AS)		Gas mmol/g AS $\times 100$						
Temp.(°C)	Time(min)	Coke	Gases	H <sub>2</sub>	CH <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>8</sub>	C <sub>2</sub> H <sub>4</sub> +C <sub>3</sub> H <sub>6</sub>	CO	CO <sub>2</sub>
440	15	27.8	2.6	44	62	15.0	7.7	7.0	4.0	1.8
	30	31.8	3.3	63	83	19.7	10.0	8.0	4.0	1.8
	60	33.8	4.4	113	123	28.3	13.7	9.4	4.3	2.0
430	15	21.9	2.0	27	50	10.7	5.3	5.0	3.3	2.0
	30	26.5	2.4	42	62	14.3	6.7	4.0	4.0	2.0
	60	29.7	3.3	71	86	20.2	9.7	8.0	4.3	2.0
420	15	2.6	1.1	20	28	6.0	2.7	1.3	3.0	1.8
	30	12.7	1.4	31	36	7.7	3.3	2.0	3.3	1.7
	60	24.4	2.1	86	56	12.0	5.7	2.7	3.3	1.9
410	15	0.0	0.7	14	19	4.0	1.7	1.4	2.3	1.8
	30	0.0	0.8	12	18	3.7	1.7	1.4	2.7	1.8
	60	3.3	1.1	27	30	6.0	2.3	1.3	3.0	1.8
400	15	0.0	0.3	3	7	1.3	0.6	0.0	1.7	1.6
	30	0.0	0.5	9	11	2.3	1.0	0.8	1.6	1.6
	60	0.0	0.7	14	18	3.7	1.3	1.0	2.0	1.8

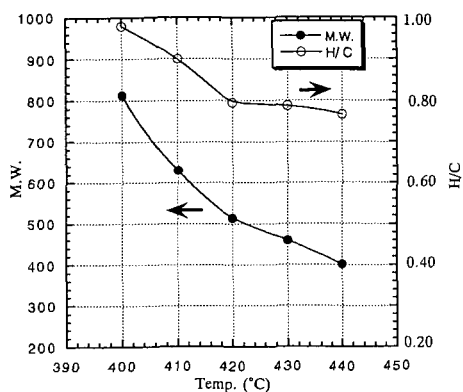


Figure 3. Effect of cracking temperature on molecular weight and H/C of reacted asphaltene

N<sub>2</sub> : 1Mpa, MLVR-AS/DH=3/15wt, React. time 60 min

Table 3 Structural Parameters of MLVR-AS and reacted asphaltene

Parameter	MLVR-AS	Cracking temp. (°C)		
		400	430	440
H/C	1.19	1.03	0.79	0.76
M.W	1730	813	459	401
Ia	0.45	0.55	0.66	0.88
Ct	128	61	35	31
Ht	152	63	28	24
Car	58	34	24	24
Har	16	10	9	9
H <sub>α</sub>	26	15	6	6
H <sub>β</sub>	83	28	10	6
H <sub>γ</sub>	27	11	3	3
M	3.0	1.5	1.0	1.0
Rt	24.0	13.0	10.0	8.0
Ra	15.0	9.0	6.0	7.0
Rn	9.0	4.0	4.0	1.0
Cap	34.0	19.0	14.0	12.0
Ctr	81.0	43.0	33.0	27.0
N	9.2	4.5	1.0	2.0
I	5.2	3.9	2.0	2.0

Ct : Number of total carbon  
 Ht : Number of total hydrogen  
 Car : Number of aromatic carbon  
 Har : Number of aromatic hydrogen  
 H<sub>α</sub> : Number of hydrogen α to aromatic rings  
 H<sub>β</sub> : Number of hydrogen β to aromatic rings  
 H<sub>γ</sub> : Number of hydrogen γ to aromatic rings  
 M : Number of fused ring units  
 Rt : Number of total rings  
 Ra : Number of aromatic rings  
 Rn : Number of naphthalenic rings  
 Cap : Number of peripheral carbon of aromatic rings  
 Ctr : Number of total carbon of fused rings  
 N : Number of paraffinic chain  
 I : Average chain length

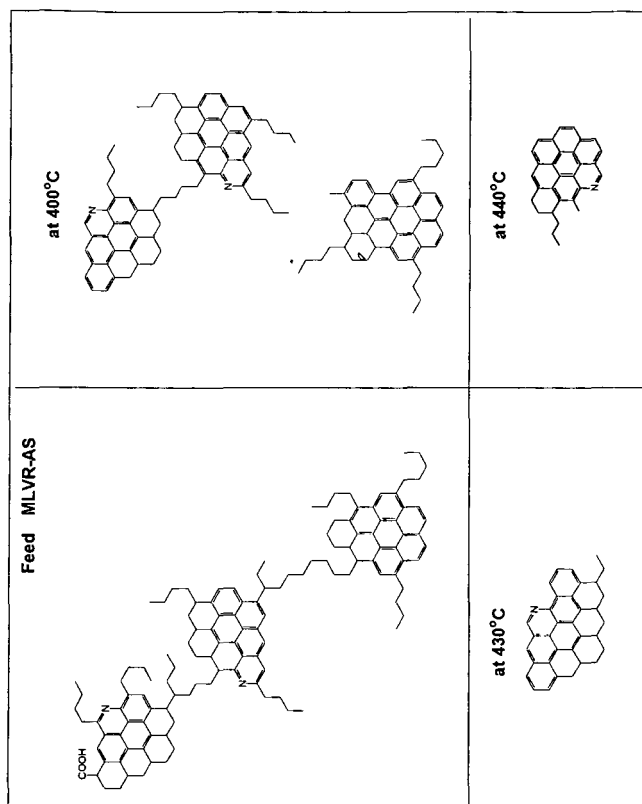


Figure 4. Structural Change of MLVR-AS in Thermal Cracking